Ice Is Wet—Water Shown to Cover its Surface

Solving a century-old puzzle, the thickness of the liquid water layer at the surface of ice has been measured precisely. Using new x-ray techniques at Berkeley Lab's Advanced Light Source (ALS), a team led by Miquel Salmeron has proved that a water layer 2 nm thick exists at the surface of ice near its melting point and that it persists at temperatures as low as −20° C. Furthermore, it was proved that surface contamination, which is ubiquitous in natural environments, strongly enhances this "premelting" of ice.

The existence of a water layer on the surface of ice at temperatures close to its melting point was first predicted by Michael Faraday in 1840. It is an important phenomenon, affecting the geology of polar ice caps, atmospheric chemistry, environmental science, and tribology. Previously, MSD researchers used surface science techniques such as low energy electron diffraction and sum frequency generation to prove that at least the outermost monolayer of ice is "wet" (Highlights 96-2, Van Hove, Somorjai and 96-11, Shen). There is, however, little agreement in the literature on the thickness of the layer, and there are only a few studies of the effect of contaminants on it.

Since ice near its melting point is in equilibrium with water vapor at pressures in the torr range and, in many cases, is exposed to ambient air, a certain degree of contamination is inevitable. Thus, in order to perform definitive studies, both the degree of molecular order and the extent of surface contamination need to be determined under the same experimental conditions. To this end, a new high-pressure electron spectrometer was developed at the ALS. In it, x-rays are focused onto an ice surface in its atmosphere of water vapor. Information about the ice surface is contained in the flux and energy spectrum of electrons that are emitted from the surface via "photoemission." In an ordinary instrument, these electrons would not get through the water vapor and would not be detected. However, by extracting the electrons via an aperture located just above the ice surface and using a specially designed electron-focusing lens (the unique feature of the instrument), sufficient numbers of electrons can be collected and measured to perform high resolution spectroscopy.

The researchers used two complementary x-ray spectroscopy techniques—near-edge x-ray absorption fine-structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS)—to measure the ice thickness and the degree of surface contamination. By starting with very pure water condensed into ice at −40° C and slowly warming up the sample to 0° C, it was observed that a thin layer of water begins to appear at −20° C and that its thickness reaches 2 nm at –2 ° C. As the ice is allowed to "age" in the sample chamber, the presence of carbon was detected in the XPS spectra, indicating that contamination from gases in the sample chamber was occurring. For example, in pure water, the water layer is about 1.5 nm thick at −4° C. When the contamination reaches a level calculated to be equivalent to only one monolayer of carbon contamination, the thickness of the water layer is doubled to 3 nm (the depth resolution of the technique).

In summary, it has been shown that the premelting of pure ice begins at −20° C in a layer up to 2 nm thick. In addition, the important role of surface contamination in enhancing the extent of premelting has been quantified for the first time. This finding is significant because organic contaminants are likely to be present on any ice surface exposed to ambient conditions. The results call for a more detailed study of the role of different types of contaminants including, for example, CO_2, which could play an important role in the chemistry of ice in the Earth's atmosphere.

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Hendrik Bluhm, , D Frank Ogletree, Charles S Fadley, Zahid Hussain, and Miquel Salmeron, "The premelting of ice studied with photoelectron spectroscopy," *J. Phys.: Condens. Matter* **14,** L227–L233 (2002).